JOURNAL OF CATALYSIS 100, 130–137 (1986)

Vanadium Poisoning of Cracking Catalysts: Mechanism of Poisoning and Design of Vanadium Tolerant Catalyst System

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Received August 22, 1985; revised February 15, 1986

The mechanism of vanadium poisoning of cracking catalysts is described. Experimental results identify the poison precursor as volatile vanadic acid, H_3VO_4 which is formed under FCC regenerator conditions by the reaction $V_2O_5(s) + 3H_2O(v) \rightleftarrows 2H_3VO_4(v)$. The concentration of H_3VO_4 in a typical regenerator (730°C, 20% H_2O, 2 atm total pressure) is 1–10 ppm. Since H_3VO_4 is a strong acid analogous to H_3PO_4, it can destroy the zeolite by hydrolysis of the zeolite SiO_2/Al_2O_3 framework. A basic solid with reasonable pore structure should be an effective scavenger. Basic alkaline earth oxides such as MgO or CaO are shown to be effective for vanadium scavenging. Microactivity testing shows excellent activity retention when 20% MgO is blended with cracking catalyst at vanadium loadings of 0.67% and 1.34% V by weight on catalyst. However, the SO_x in the regenerator flue gas can form a sulfate that competes with the formation of the vanadate. The degree of competition will be thermodynamically controlled. Since the formation of the vanadate from the oxide expands the lattice, pore structure effects exist similar to those observed for the reaction of calcium oxide with sulfur oxides. © 1986 Academic Press, Inc.

INTRODUCTION

The effects of vanadium and nickel contaminants on the performance of cracking catalysts are well known (*1, 2*). In general, a loss of both activity and selectivity is observed as metal levels deposited on the catalyst increase from 2000 to 10,000 ppm. Residual feedstocks have significant amounts of Ni and V and the presence of these contaminants represents a major obstacle to processing large amounts of residual oil. The metals are found in the residual oil as complexes with porphyrins (*3*) or other material and are deposited quantitatively on the catalyst with the coke during the cracking reaction. Fluid catalytic cracking catalysts for the production of gasoline are generally composed of a rare earth exchanged Y-type zeolite imbedded in a silica–alumina matrix. Nickel greatly increases the gas (H_2) and coke production of the catalyst, while vanadium reduces both catalyst activity and selectivity by destroying zeolite crystallinity and producing increased gas (H_2) and coke.

Currently, antimony is used to control nickel poisoning in a process developed by Phillips (*4*). Vanadium poisoning has been a more difficult problem. In an effort to reduce the poisoning effect of vanadium, some refineries have proposed various hardware changes (*5, 6*). Tin has been used commercially for processing high-metal feedstocks. Patents which claim the use of tin either deposited on the catalyst from the feedstock or by impregnation (*7*) or by adding a tin-containing diluent to the catalyst inventory (*8*) have been issued to Gulf. Some common methods of reducing the effect of catalyst poisoning are to increase usage rates or to use a more active, stable catalyst. These methods can be expensive, may involve catalyst disposal problems, and are not especially effective.

In this paper a mechanism for vanadium poisoning is proposed, and based on the proposed mechanism, the design of a vanadium scavenger is described.

EXPERIMENTAL

The cracking catalyst used in this work is a laboratory-prepared catalyst composed of

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TABLE 1

Properties of Catalyst

20% REY	
80% SiO_2/Al_2O_3/Kaolin matrix	
Al_2O_3	31.7%
Na_2O	0.65%
RE_2O_3	3.15%
Surface area	152 m^2/g
Pore volume	0.22 cm^3/g

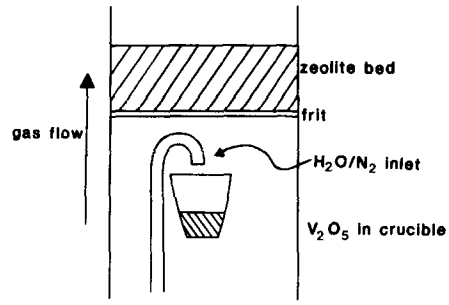

FIG. 1. Schematic of flowing tube reactor for exposure experiments.

20% zeolite imbedded in 80% SiO_2–Al_2O_3–Kaolin matrix. Typical properties of the catalyst are shown in Table 1. The surface area of the matrix is ~30 m^2/g with the remainder being zeolite as measured by single point BET. The zeolite may be an ultrastable Y zeolite prepared by procedure A (*9*, p. 320) or a rare earth exchanged Y zeolite (REY) with 3.2% Na_2O. The REY may be calcined and exchanged to low Na_2O (0.9% Na_2O). The SiO_2/Al_2O_3 ratio of the REYs is 5/1.

The metal impregnation procedure used is similar to that described by Mitchell (*10*). The catalyst is impregnated to appropriate weight percentage V on catalyst to incipient wetness using vanadyl naphthenate with oil as a solvent, or vanadyl oxalate with water as a solvent. The catalyst is then calcined at 760°C for 4 h with dry air to burn off the organics. In other experiments V_2O_5 powder is physically blended with catalyst to give equivalent weight percentage V on catalyst. Typically, the catalyst is then given a steam treatment in a fixed bed at 732°C for 8 h at 2 atm 100% H_2O pressure. The activity of the catalyst with or without metal impregnation is tested by a MAT test similar to the ASTM-3907-80 procedure. The conditions of the test are 498°C, catalyst-to-oil ratio nominally = 3, WHSV (h^{-1}) = 16, and the feedstock is a West Texas Heavy Gas Oil boiling range 320–500°C.

Steaming exposure experiments were performed in a fluid bed high temperature reactor. A schematic of the Inconel tube reactor is shown in Fig. 1. The diameter of the tube reactor is 3.5 in. and is mounted vertically in a tube furnace. The zeolite bed rests on a 20-μm frit. Three heating zones are temperature controlled to ±3°C at 750°C. A thermocouple is inserted into the zeolite bed to monitor the bed temperature. The system pressure is controlled by a back pressure regulator and is measured using a Wallace–Tiernan gauge downstream. N_2 gas is used as the carrier gas and the flow rate of N_2 is monitored by a wet test meter located at the discharge of the back pressure regulator. H_2O partial pressure is generated by a heated temperature-controlled H_2O vessel upstream from the reactor. N_2 flow bubbles through the H_2O vessel into the reactor. The H_2O vapor is condensed prior to the back pressure regulator. Figure 1 shows that V_2O_5 can be placed in a crucible and allowed to react with the inlet gas stream prior to flowing through the zeolite bed. The conditions of the exposure experiments are shown in Table 2. X-Ray powder

TABLE 2

Conditions of Exposure Experiments

P_{system}	2 atm
P_{H_2O}	1 atm
T	750°C
N_2 flow	100–150 cm^3/min
Zeolite weight	100 g
Exposure time	72 h

diffraction spectra of the zeolite after exposure are obtained using a Philips diffractometer and the spectra are digitized and stored by a computer. Surface area measurements of the zeolite are standard five point BET measurements made in the range $P_0/P = 0.01–0.6$. The zeolite used in these experiments is a calcined REY NH_4^+ exchanged to 0.9% Na_2O. The zeolite was precalcined for 2 h at 538°C to remove physisorbed H_2O prior to loading into the reactor.

Electron microprobe vanadium profiles are obtained by dispersing the $SiO_2–Al_2O_3$ catalyst powder (28% SiO_2, 72% Al_2O_3 surface area = 300 m^2/g) in an epoxy resin disk. The disks are ground to expose catalyst cross sections and vapor coated with carbon. The vanadium profiles of the catalyst cross sections are obtained on a Cameca MBX wavelength dispersive microprobe using a focused-spot electron beam at 20 keV.

MgO used in blending experiments is 99.5% pure with a surface area of 30 m^2/g.

RESULTS AND DISCUSSION

Mechanism of Poisoning by Vanadium

An examination of the laboratory impregnation procedure yields important insights into the mechanism of vanadium poisoning. This laboratory impregnation procedure was first developed by Mitchell (*10*) to mimic field performance of cracking catalysts and with minor variations is used throughout the industry. The catalyst is impregnated to incipient wetness with an appropriate vanadium compound such as V naphthenate or oxalate. The organics are then burned off at 760°C in dry air. MAT results in Table 3 show that no deactivation occurs after this step and typical activities and selectivities of fresh (not steamed) catalyst are observed. Only after a steam treatment does deactivation occur. It has been suggested that a $RE_2O_3–V_2O_5$ eutectic lowers the melting point of zeolite causing zeolite destruction by sintering (*11*). One would expect that catalyst deactivation would occur during a dry air calcination if a eutectic formation was responsible for zeolite destruction, since 760°C is well above the melting point of V_2O_5 (670°C). This suggests that the presence of high temperature H_2O vapor is necessary for catalyst deactivation.

TABLE 3

Laboratory Impregnation Procedure

Step 1	Impregnate the catalyst to incipient wetness with vanadyl naphthenates in oil or oxalate in water with the desired level of V		
Step 2	Calcine for 4 h at 760°C in dry air		
		0% V	0.34% V
	MAT (vol% conversion)	79	79
	H_2/C (wt%)	0.14/10	0.4/14.5
Step 3	Calcine for 8 h at 732°C, 2 atm H_2O		
		0% V	0.34% V
	MAT (vol% conversion)	76	40
	H_2/C (wt%)	0.04/3.2	0.22/3.2

This is further demonstrated by an experiment where vanadium oxalate is impregnated on a 20% zeolite/80% $SiO_2–Al_2O_3$ matrix sample and calcined in dry air at 760°C for 2 h. The sample is then split into two parts. One part is steamed at 760°C for 5 h in 100% steam, and the other part is calcined in dry air at 760°C for 5 h. The results in Table 4 show significant differences in deactivation. Catalysts with impregnated vanadium have no loss of activity or of zeolite content after calcination in dry air at 760°C. After steaming, all vanadium-impregnated samples deactivated severely, with the higher soda material deactivating the most severely. Surface area and XRD measurements show the same result, a nearly complete loss of zeolite in the presence of 0.5% V only under steam conditions. The results for a catalyst containing USY are similar to results with rare earth stabilized zeolites, except that without va-

TABLE 4

Vanadium Deactivation of 20% Sieve Catalysts as Measured by Surface Area, MAT Activity, and XRD Peak Height

Zeolite	Catalyst sample				
	As prepared	Deactivated 5 h, 760°C			
		Dry air		100% Steam	
		0% V	0.5% V	0% V	0.5% V
20% REY[a]					
MAT (% Conv.)	84	86	81	74	22
S.A. (m^2/g)	203	—	191	—	51
% Crystallinity	23	—	16	—	0
20% Low soda calcined REY[b]					
MAT (% Conv.)	82	85	83	74	63
S.A. (m^2/g)	183	—	191	—	103
% Crystallinity	20	—	16	—	3
20% Low soda USY					
MAT (% Conv.)	83	85	84	72	40
S.A. (m^2/g)	175	—	183	—	83
% Crystallinity	20	—	12	—	2

[a] % Na_2O = 3.7.
[b] % Na_2O = 0.9.

nadium and with steam the USY deactivates by dealumination without a large loss of zeolite, while with 0.5% vanadium a nearly complete loss of zeolite is observed, similar to that of the samples containing the rare earth stabilized zeolite.

Steam is also necessary to distribute vanadium through the catalyst particle. A porous silica–alumina particle was prepared with 10% zeolite according to Ref. (*12*, example 2). Figure 2 shows a vanadium electron microprobe profile after impregnation with vanadium and subsequent calcination. Figure 3 shows the vanadium profile after steam deactivation. The impregnation procedure using vanadium naphthenate in oil distributes the vanadium throughout the particle. During calcination the vanadium

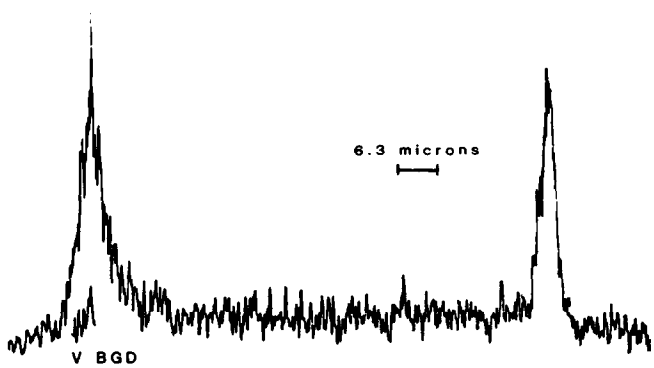

FIG. 2. Electron microprobe vanadium profile of a zeolite containing silica alumina catalyst (*12*) after laboratory impregnation and air calcination, but before steam treatment.

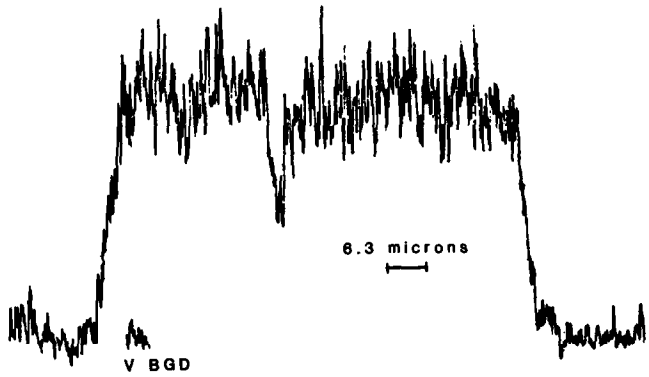

FIG. 3. Electron microprobe vanadium profile of a zeolite containing silica alumina catalyst after laboratory impregnation, air calcination, and steam deactivation, 732°C, 2 atm steam, 8 h.

migrates to the outer skin of the porous particle, and only after steam deactivation is the vanadium observed to attack the zeolite throughout the catalyst particle.

The importance of the steam treatment for vanadium poisoning is further illustrated by an alternative deactivation procedure. Instead of impregnating the vanadium from a liquid system, V_2O_5 powder is physically blended with the catalyst powder. The data in Table 5 show that the catalyst is deactivated after steam treatment without a prior calcination. Only 0.6 g V_2O_5 is blended with 99.4 g of catalyst, with the same percentage V used in the impregnation experiment, and after steam treatment deactivation occurs to a similar extent. Only one conclusion can be drawn from these experiments: the poison precursor for vanadium deactivation must be volatile. Liquid wetting or some other liquid- or solid-state reaction cannot account for deactivation from small amounts of V_2O_5 powder, or for the failure of V_2O_5 to deactivate catalysts after a dry calcination.

To prove that zeolite destruction is caused by a volatile vanadium species, steam exposure experiments were carried out in a flowing tube reactor. Figure 4a shows the powder pattern of the REY prior to loading in the reactor. Figure 4b shows the powder pattern after exposure only to H_2O/N_2 (1 atm H_2O) for 72 h at 750°C (no V_2O_5 in crucible). Figure 4c shows the powder pattern after 72 h exposure when V_2O_5 is placed in the crucible and H_2O/N_2 are made to flow under the same conditions as above. As evidenced by Fig. 4c, the zeolite completely loses crystallinity verified by a surface area of 41 m^2/g.

Hence, the poison precursor for vanadium poisoning must involve H_2O vapor and V_2O_5 and must be volatile. Compounds of vanadium with oxidation states lower than +5 are not considered since the conditions of the regenerator are highly oxidizing. Two oxyvanadium species are possible.

$$V_2O_5(s) + H_2O(v) \rightleftarrows 2VO_2(OH)(v) \quad (1)$$

$$V_2O_5(s) + 3H_2O(v) \rightleftarrows 2VO(OH)_3(v). \quad (2)$$

Reaction (2) is more probable since vanadium is a transition metal and high coordi-

TABLE 5

The Result of Steam Deactivation (732°C, 8 h, 2 Atm H_2O) of a Catalyst (20% REY, 80% Silica–Alumina Clay Matrix) Physically Blended (0.34% V) with V_2O_5 Powder

	0% V	0.34% V
MAT (vol% Conversion)	67	40
H_2 (wt% in feed)	0.04	0.11
C (wt% in feed)	2.5	3.6

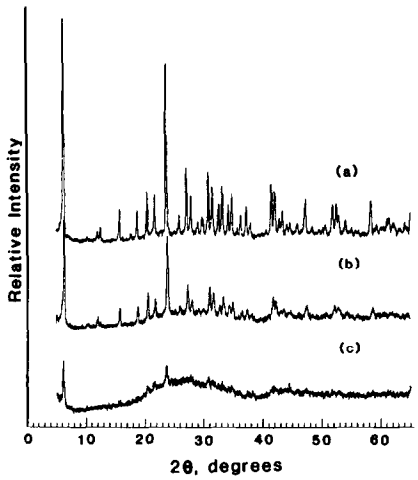

FIG. 4. X-Ray powder spectra of REY (0.9% Na_2O) in exposure experiments (a) after 539°C for 2 h prior to loading in reactor, (b) after 1 atm H_2O partial pressure (total pressure 2 atm) for 72 h, (c) after 1 atm H_2O partial pressure (2 atm total pressure) with V_2O_5 in crucible for 72 h.

nations are favored. There is also thermochemical evidence for $VO(OH)_3$ being formed from the reaction of V_2O_5 with H_2O. Yannopoulos (*13*) has determined the equilibrium vapor pressure of the V_2O_5–H_2O system at various temperatures using a flowing tube reactor. In that work the equilibrium constant for reaction (2) as a function of temperature was measured to be

$$\log K_p = 9619.1(\pm 116.0)/T - 0.225 \pm 0.023. \quad (3)$$

For a typical FCC regenerator temperature at 970 K (1285°F), K_p for this reaction is 7.22×10^{-11}. A typical water partial pressure of 0.4 atm (20% steam at 2 atm total pressure) yields an equilibrium vapor pressure of 2.15×10^{-6} atm for $VO(OH)_3$ or ~1 ppm. Since FCC regenerator temperatures vary from 950 to 1000 K the concentration of $VO(OH)_3$ at 20% H_2O will vary from 1 to 10 ppm.

It can be inferred by analogy with phosphoric acid that $VO(OH)_3$ will be a strong acid. We will refer to $VO(OH)_3$ as vanadic acid with the formula H_3VO_4. Since Y-type zeolites with Si/Al ratio = 2.5 are known to be unstable to acid (*9*), it is reasonable that H_3VO_4 destroys zeolite crystallinity (and activity) by high temperature acid-catalyzed hydrolysis with the presence of steam in the regenerator.

The mechanism of vanadium poisoning of cracking catalysts can be summarized as follows: Vanadium is present in the oil as VO_2^+ porphyrins. The vanadium is deposited on the catalyst with coke. In the regenerator the coke is burned off, and the vanadium is oxidized to V_2O_5. Several reactions are possible. V_2O_5 may deposit on the catalyst matrix and in this form will not destroy zeolite. The V_2O_5 can react with H_2O vapor present in the regenerator, forming vanadic acid. Vanadic acid reacts with the zeolite and destroys crystallinity, reducing catalyst activity. The vanadic acid may also react with the catalyst matrix. After destruction of the zeolite, the V_2O_5 may combine with rare earth compounds left as debris. The formation of rare earth vanadates has been previously described (*11*).

Design of a Vanadium Scavenger

A material which will effectively scavenge H_3VO_4 before it reacts with the zeolite must have a sticking coefficient for reaction with H_3VO_4 that is much greater than that for the reaction with zeolite. Since H_3VO_4 is a strong acid the obvious choice is a basic oxide such as alkaline earths. The calculated equilibrium constant from the thermochemical data (*14*) strongly favors the formation of vanadates at 677°C (970 K) by reaction of MgO or CaO with H_3VO_4.

$$2MgO(s) + 2H_3VO_4(v) \xrightleftharpoons{K(970\ K) = 2.58 \times 10^{19}} Mg_2V_2O_7(s) + 3H_2O(v) \quad (4)$$

$$2CaO(s) + 2H_3VO_4(v) \xrightleftharpoons{K(970\ K) = 6.78 \times 10^{26}} Ca_2V_2O_7(s) + 3H_2O(v). \quad (5)$$

Alkali oxides are less suitable scavengers for H_3VO_4 because of their well-known deleterious effects on cracking catalysts (*15*). Table 6 shows vanadium deactivation MAT

TABLE 6

Performance of MgO Blended with Cracking Catalyst (20% REY, 80% Silica/Clay Matrix)

	MAT (% conversion)		Coke and gas (H_2) selectivity (wt%) of feed			
	0% MgO	20% MgO	0% MgO		20% MgO	
			H_2	Carbon	H_2	Carbon
0% V	72	67	0.06	2.2	0.06	2.3
0.34% V	40	—	0.11	3.2	—	—
0.67% V	14	55	0.22	0.8	0.05	1.8
1.34% V	—	40	—	—	0.11	1.5

data when MgO powder is physically blended with cracking catalyst. Catalysts blended with 20% MgO at 1.34% vanadium have improved selectivity for gas and coke and have the same activity as the catalyst without MgO at 0.34% vanadium. These results imply that a refiner could quadruple the vanadium level on the catalyst and maintain activities and selectivities.

Simply adding MgO or CaO to a FCC unit is not suitable since these particles are inherently soft and light. They would attrit and be elutriated from the unit before reasonable levels of MgO could be accumulated in the circulating catalyst inventory. Depending on the vanadium level, between 5 and 20% of the scavenger is required in inventory to effectively inhibit vanadium poisoning. Consequently, it is required that the catalyst additive be physically hard enough to be retained in a FCC unit.

The scavenger also needs to have a high capacity for vanadium, a property related to the pore structure of the material. The partial molar volume of MgO is 11 cm^3/mole, while the partial molar volume of $Mg_2V_2O_7$ is approximately 86 cm^3/mole, based on the pyrochlore structure. This represents an eightfold expansion as the vanadate is formed. If the pores of MgO are small, the pores will quickly plug and decrease the further reaction of H_3VO_4 with MgO. After the pores are plugged, further reaction of H_3VO_4 is governed by a relatively slow solid-state diffusion. Large pores, high pore volume, and high surface area, therefore, favor improved scavenging. Preliminary experiments indicate that MgO must have a pore volume greater than 0.1 cm^3/g, and that the average pore diameter must be greater than 400 Å for effective vanadium scavenging at high vanadium levels. Similar pore structure effects have been described for the reaction $CaO + SO_3 \rightleftarrows CaSO_4$ (*16*).

Poisoning of the scavenger can occur due to the presence of sulfur oxides in the flue gases of the regenerator. The SO_3 can react with the alkaline earth oxides to form sulfates in competition with H_3VO_4. The equilibrium constants for the reactions of $MgSO_4$ and $CaSO_4$ with vanadic acid calculated from thermodynamic data (*14*) are

$$2CaSO_4(s) + 2H_3VO_4(v) \xrightleftharpoons{K(970\ K) = 472.5\ atm^3} Ca_2V_2O_7(s) + 2SO_3(v) + 3H_2O(v) \quad (6)$$

$$2MgSO_4(s) + 2H_3VO_4(v) \xrightleftharpoons{K(970\ K) = 6.675 \times 10^5\ atm^3} Mg_2V_2O_7(s) + 2SO_3(v) + 3H_2O(v). \quad (7)$$

Assuming a worst case in which all the SO_x is assumed to be SO_3 at a level of 2000 ppm in the regenerator with 20% H_2O and 1 ppm H_3VO_4 and at the relatively low temperature of 970 K, the quantity $(SO_3)^2(H_2O)^3$/

$(H_3VO_4)^2$ can be calculated as

$$\frac{[SO_3]^2[H_2O]^3}{[H_3VO_4]^2} = 2.215 \times 10^5 \text{ atm}^3 \quad (8)$$

and compared to the equilibrium constant. The equilibrium constant, in the case of calcium (Eq. (6)), is much smaller than $[SO_3]^2[H_2O]^3/[H_3VO_4]^2$ and the formation of calcium sulfate is favored. The opposite is true for the case with magnesium (Eq. (7)), and magnesium vanadates are favored. In very high temperature regenerators, 1060 K (1450°F), the formation of $Ca_2V_2O_7$ becomes more favorable, and the performance of a CaO-based scavenger will improve. At current practical regenerator temperatures, $Mg_2V_2O_7$ is favored and, consequently, a magnesium oxide-based vanadium scavenger is preferred.

An effective vanadium scavenger for use in FCC units must have all the typical physical properties of standard cracking catalysts: bulk density, attrition resistance, correct particle size distribution, etc. These properties are not entirely compatible with, for example, the optimum pore structure, and some degree of compromise must be achieved. A material meeting the various requirements has been described (*17*).

REFERENCES

1. Ritter, R. E., Rheaume, L., Welsh, W. A., and Magee, J. S., *Oil & Gas J.*, 103 (July 6, 1981).
2. Jaras, S., *Appl. Catal.* **2,** 207 (1982).
3. Agrawal, B. B., and Gulati, F. B., *Pet. Hydrocarbons* **6,** 193 (1972).
4. Gall, J. W., Nielsen, R. H., McKay, D. L., and Mitchell, N. W., paper presented at 1982 NPRA Annual meeting, San Antonio, Tex.; McKay, D. L. *Hydrocarbon Process.*, 97 (Sept. 1977).
5. Zandona, O. J., Busch, L. E., Hettinger, W. P., Jr., and Krock, R. P., *Oil & Gas J.*, 82 (March 22, 1982).
6. Dean, R., Mauleon, J. L., and Letzsch, W. S., *Oil & Gas J.*,75 (Oct. 4, 1982); 168 (Oct. 11, 1982).
7. Mitchell, B. R., and Swift, E. S., U.S. Patent 4,101,417 (1978).
8. Ocelli, M. L., and Swift, E. S., U.S. Patent 4,466,884 (1984).
9. McDaniel, C. V., and Maher, P. K., *in* "Zeolite Chemistry and Catalysis" (J. A. Rabo, Ed.), ACS Monograph 171. Amer. Chem. Soc., Washington, D.C., 1976.
10. Mitchell, B. R., *Ind. Eng. Chem. Prod. Res. Dev.* **19,** 209 (1980).
11. Pompe, R., Jaras, S., and Vannerberg, N-G, *Appl. Catal.* **13,** 171 (1984).
12. Chiang, R. L., and Seese, M. A., U.S. Patent 4,499,197 (1985).
13. Yannopoulos, L. N., *J. Phys. Chem.* **72,** 3293 (1968).
14. Dean, J. A. (Ed.) "Lange's Handbook of Chemistry," 12th ed. McGraw–Hill, New York, 1979.
15. Letsch, W. S., and Wallace, D. N., *Oil & Gas J.*, 56 (Nov. 29, 1982).
16. Bhatia, S. K., and Perlmutter, D. D., *AIChE J.* **27,** 226 (1981).
17. Wormsbecher, R. F., Peters, A. W., and Maselli, J. M., paper presented at Ninth North American Catalyst Society Meeting, Houston, Tex., March 18–21, 1985.